

CLAIMS

What is claimed is:

- 5 1. A process for producing particulate titanium dioxide comprising:
  - a) mixing an alkaline-reacting liquid with an aqueous solution of titanyl sulfate at elevated temperature until the resultant mixture reacts acidically and is neutralized to a pH  
10 between 5 and 9, forming flocculates of titanium dioxide nanoparticles;
  - b) first-isolating the formed titanium dioxide nanoparticle flocculate;
  - c) first-washing in water the isolated titanium dioxide  
15 nanoparticle flocculate;
  - d) second-washing in an acid or an alkali the isolated and first-washed nanoparticle flocculate,
  - e) second-isolating as a product of the second-washing an acidic or an alkaline titania concentrate of particulate titanium  
20 dioxide.
2. The process for the producing particulate titanium dioxide according to claim 1 extended and enlarged to a process of producing a sol of particulate titanium dioxide comprising as a  
25 step after the e) second-isolating the further step of:
  - f) dispersing the second-isolated titania concentrate in a polar sol-forming medium to make a sol suitable to serve as a

coating in which is present particulate titanium dioxide.

3. The extended and enlarged process of producing both (i) particulate titanium dioxide and (ii) a sol of particulate titanium dioxide according to claim 2

wherein the a) mixing through f) dispersing makes a sol that is transparent.

4. The extended and enlarged process of producing both (i) particulate titanium dioxide and (ii) a sol of particulate titanium dioxide according to claim 2 still further extended and enlarged to use the sol as a coating, the method comprising as a step after the f) dispersing the further step of:

g) applying a film of the titania sol to a surface.

5. The process according to claim 4 further comprising as a step after the g) applying,

h) neutralizing the surface with a suitable acidic- or alkaline-reacting compound; and

i) washing the surface with water.

6. The process according to claim 4 wherein the surface is prepared after the g) applying of the film of the titania sol by:

coating said surface with 0.1 to 1,000 wt., relative to  $\text{TiO}_2$ , that is within the titania sol in the g) applying step, of at least one oxide, hydroxide or hydrous oxide compound drawn from the group consisting of aluminum, silicon, zirconium, tin,

magnesium, zinc, cerium and phosphorus.

7. The process according to claim 6 wherein the coating with at least one oxide, hydroxide or hydrous oxide compound is 5 to 200 wt. %, relative to the  $\text{TiO}_2$ .

8. The process according to claim 5 wherein after the coating the surface is dried.

9. The process according to claim 5 wherein after the coating the surface is annealed.

10. The process according to claim 1 wherein the mixing is until the resultant mixture reacting acidically is neutralized to a pH between 6.5 and 7.5.

11. The process according to claim 1 wherein the mixing is with an alkaline-reacting liquid drawn from the group consisting essentially of aqueous solutions of ammonium hydroxide, sodium hydroxide, and potassium hydroxide.

12. The process according to claim 1 wherein the mixing is with an alkaline-reacting liquid drawn from the group consisting essentially of carbonates of sodium, potassium and ammonium.

13. The process according to claim 1 wherein the mixing is with

an ammonium hydroxide solution having a concentration from 1 to 8 molar  $\text{NH}_4\text{OH}$ .

14. The process according to claim 1 wherein the mixing proceeds  
5 at a temperature within the range of  $60^\circ\text{C}$  to  $100^\circ\text{C}$ .

15. The process according to claim 1 wherein, between the a) and the b) first-isolating transpires the further step of

a1) letting cool a mixture created by the a) mixing.

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16. The process according to claim 15 wherein the a1) letting cool the mixture comprising:

quenching to a temperature below  $60^\circ\text{C}$  for greater than  $1/4$  hour.

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17. The process according to claim 1 wherein the b) first-isolating comprises:

separating, by filtering or other method conventionally recognized in the art.

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18. The process according to claim 17 wherein the d) second-washing in the acid or the alkali is with monobasic acid or alkali so as to both (i) remove contaminants from the isolated and first-washed nanoparticle flocculate and (ii) introduce ions  
25 necessary for sol formation.

19. The process according to claim 18 wherein the d) second-washing is in monobasic acid or alkali 1 to 6 times the weight of the titanium flocculate precipitate.

5 20. The process according to claim 18

wherein the d) second-washing in the acid or the alkali is with hydrochloric acid.

21. The process according to claim 20

10 wherein the d) second-washing in the acid or the alkali is with 3 to 6 molar hydrochloric acid.

22. The process according to claim 1

15 wherein the e) second-isolated acid or alkaline titania concentrate contains 4 to 40 wt. % of  $\text{TiO}_2$ , the remainder being any of (i) wash acid or wash alkali, (ii) water moisture and (iii) small quantities of contaminants.

20 23. The process according to claim 2 wherein the f) dispersing of the second-isolated titania concentrate in a polar sol-forming medium is so to make a transparent sol in which  $\text{TiO}_2$  is present exclusively as nano-particles having a diameter of between 1 and 100 nm.

25 24. The process according to claim 2 wherein the f) dispersing of the second-isolated titania concentrate is in a polar sol-forming medium consisting essentially of water, or an alcohol

containing 1 to 10 carbon atoms and at least one hydroxide group per molecule, or mixtures thereof.

25. A sol suitable as a coating consisting essentially of

5 titanium dioxide nanoparticles educed from

an aqueous titanyl sulfate solution

neutralized with an alkali to

precipitate titania floculates that are

water-washed and then

10 acid-washed; dispersed in

a polar sol-forming medium.

26. The sol according to claim 25

wherein the sol is transparent.

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27. The sol according to claim 25 wherein the aqueous titanyl sulfate solution from which the titanium dioxide nanoparticles are educed contains sulfuric acid.

20 28. The sol according to claim 25

wherein the titanyl sulfate solution is obtained by

digesting with sulfuric acid material drawn from the group consisting of ilmenite and titanium slag;

dissolving a digestion cake resultant from the digesting in water; and

performing clarification to derive the aqueous titanyl sulfate solution suitable as an educt.

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29. The sol according to claim 25 wherein the titanyl sulfate undergoing dissolution in water is commercial grade.

30. The sol according to claim 25

10        wherein the titanyl sulfate solution is obtained by dissolution of titanium dioxide and  $\text{TiO}_2$  hydrates, including orthotitanic acid and metatitanic acid, in sulfuric acid ( $\text{H}_2\text{SO}_4$ ).

31. The sol according to claim 25

15        wherein the titanyl sulfate solution is obtained by dissolution in  $\text{H}_2\text{SO}_4$  of alkali metal and magnesium titanates in hydrous form.

32. The sol according to claim 25

20        wherein the titanyl sulfate solution is obtained by reaction of  $\text{TiCl}_4$  with  $\text{H}_2\text{SO}_4$  to form  $\text{TiOSO}_4$  and  $\text{HCl}$ .

33. The sol according to claim 25 wherein the titanyl sulfate solution contains 100 to 300 g of titanium/l, calculated as  $\text{TiO}_2$ .

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34. The sol according to claim 25 wherein the titanyl sulfate solution contains 170 to 230 g of titanium/l, calculated as  $\text{TiO}_2$ .

35. The sol according to claim 25 having less than 0.1 wt. % of  
5 carbon.

36. A composite body exhibiting a photocatalytic effect consisting essentially of

a core particle consisting essentially of a material without  
10 deleterious effect on a photocatalytic reaction; and

a multiplicity of nanoparticles, each less than 33% the diameter of the core particles, of photocatalytic material upon the surface of the core particle, the photocatalytic material being less than 20% by weight of (i) the combined multiplicity of  
15 photocatalytic material nanoparticles and (ii) the core particle.

37. The composite body according to claim 36

wherein the core particle is less than 1 centimeter in diameter; and

20 wherein each of the multiplicity of nanoparticles is of diameter less than 100 nanometers.

38. The composite body according to claim 36 wherein the core particle's material without deleterious effect on a  
25 photocatalytic reaction consists essentially of

a material drawn from the group consisting essentially of silicates and carbonates including silicate and carbonate



powders, mineral and mineral composites including calcined clay and wollastonite, metal oxides including zinc oxide, inorganic pigments, and construction aggregates including roofing granules.

- 5 39. The composite body according to claim 36 wherein the core particle consists essentially of

a polymer.

40. The composite body according to claim 39 wherein the core  
10 particle's polymer consists essentially of

polymer drawn from the group consisting essentially of  
acrylics, acrylonitriles, acrylamides, butenes, epoxies,  
fluoropolymers, melamines, methacrylates, nylons, phenolics,  
polyamids, polyamines, polyesters, polyethylenes, polypropylenes,  
15 polysulfides, polyurethanes, silicones, styrenes, terephthalates,  
vinyls.

41. The composite body according to claim 39

wherein the polymer core particle is less than 1 centimeter  
20 in diameter.

42. The composite body according to claim 36

wherein the photocatalytic material of the multiplicity of  
nanoparticles is drawn from the group of metal compound  
25 semiconductors consisting essentially of titanium, zinc, tungsten  
and iron, and oxides of titanium, zinc, tungsten and iron, and  
strontium titanates.

43. The composite body according to claim 42

wherein the metal compound semiconductor photocatalytic material is combined with a metal or metal compound drawn from the group consisting of vanadium, iron, cobalt, nickel, copper, zinc, ruthenium, rhodium, silicon, tin, palladium, gold, platinum, and silver.

44. The composite body according to claim 36

wherein the photocatalytic material is drawn from the group of metal compound semiconductors consisting essentially of anatase titanium dioxide and zinc oxide.

45. The composite body according to claim 36

wherein the photocatalytic material consists of particles of a diameter from 1 nanometer to 100 nanometers.

46. The composite body according to claim 36

wherein the photocatalytic material consists of particles of diameter from 1 nanometer to 50 nanometers.

47. The composite body according to claim 36

wherein the photocatalytic material consists of particles of diameter from 1 nanometer to 10 nanometers.

48. The composite body according to claim 36

wherein the core particles consist of particles of diameter from 100 nanometers to 1 centimeter.

49. The composite body according to claim 36

5 wherein weight of the photocatalytic material of the combined multiplicity of nanoparticles is less than 10% of weight of the core particle.

50. A great multiplicity of composite bodies in accordance with  
10 claim 36 incorporated in amount from 0.001% to 85% by volume within a composition suitable for use as an additive or a coating.

51. The great multiplicity of composite bodies in accordance  
15 with claim 50 incorporated in a composition that further includes one or more materials from the group of building materials consisting of concrete, cement, ceramic, stucco, hard flooring, masonry, roofing shingles, wall shingles, building siding and swimming pool surfaces.

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52. The great multiplicity of composite bodies in accordance with claim 50 incorporated in a composition that is effective as an anti-fouling coating.

25 53. The composite body according to claim 36 effective in killing by contact any of algae, bacteria, mold or fungus.

54. The composite body according to claim 36 wherein, at a proportion by weight of the photocatalytic material in the composite particle of less than 10%, the efficacy of the photocatalytic material within the composite particle to kill by  
5 contact algae, bacteria, mold, and fungus upon the composite particle's surface is at least one-half (.5) as good as is the efficacy of this same photocatalytic material to kill in purest form, making that at least equal killing effect is realized with a five to one (5:1) reduction in the amount of photocatalytic  
10 material when this photocatalytic material is upon the surface of the composite particle.

55. A method of making composite photocatalytic particles comprising:

15 preparing an aqueous slurry of first particles, consisting essentially of a material without deleterious effect on photocatalytic reaction, having an associated first particle size in the range from 100 nanometers to 1 centimeter diameter;

adding a colloidal suspension of 0.1% to 60% by weight  
20 second particles, which second particles consist essentially of photocatalytic material having diameters in the range from 1 to 100 nanometers, the combined weight of second particles in the colloidal suspension being less than 20% of the combined weight of the first particles that are also within the aqueous slurry;

25 mixing the aqueous slurry and the colloidal suspension so that the photocatalytic material second particles attach through van der Waals or fusion chemical forces to the nondeleterious material first particles, forming a slurry of composite particles wherein the relatively smaller photocatalytic material second  
30 particles (i) are upon the surfaces of the relatively larger nondeleterious material first particles, and (ii) are in weight

less than 20% of these first particles.

56. The method according to claim 55

wherein the colloidal suspension added is from 0.1% to 60%  
5 by weight second particles.

57. The method according to claim 56

wherein the colloidal suspension added is of the highest  
solids concentration at which the suspension is stable, being in  
10 the range from 14% to 50% by weight.

58. The method according to claim 56 further comprising:

adjusting the pH of the mixing so as to move away from, in  
the same direction, the respective isoelectric points of the  
15 photocatalytic material second particles and the nondeleterious  
material first particles, the isoelectric points being those  
points at which the particles have a neutral net charge.

59. The method according to claim 56 further comprising:

20 adjusting the pH of the mixing so that either the  
photocatalytic material second particles or the nondeleterious  
material first particles approach their respective isoelectric  
points, but only when the mixture of both particles have low  
ionic strength and the pH is such that both particles are above  
25 or below their isoelectric points.

60. The method according to claim 56 further comprising:

establishing an opposite electrical charge on the nondeleterious material first particles and the photocatalytic material second particles.

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61. The method according to claim 56 wherein either the adding of the colloidal suspension of second particles, or the mixing of the aqueous slurry and the colloidal suspension, or both the adding and the mixing, transpires in the presence of at least one  
10 dispersant.

62. The method according to claim 56 further comprising one or more finishing steps drawn from the group consisting of separating, washing and drying the composite photocatalytic  
15 particles.

63. The method according to claim 56 further comprising drying the slurry of composite photocatalytic particles; and annealing in a kiln the dried composite photocatalytic  
20 particles.

64. The method according to claim 63 that, after the annealing, further comprises:

rapidly cooling the annealed composite photocatalytic  
25 particles to ambient room temperature within a time period, which time period is necessarily dependent upon the temperature of the annealing and the amount of the composite photocatalytic

particles, that is less than six hours.

65. The method according to claim 64 wherein the rapid cooling of the annealed composite photocatalytic is accomplished by rapid  
5 removal of the material from the kiln to a room temperature environment.

66. A photocatalytic aggregate particle consisting essentially of

10 an extender particle of material both non-photocatalytic and non-interfering with photocatalytic reaction; with

discrete photocatalytic titanium oxide particles exposed on the surface.

15 67. The photocatalytic aggregate particle according to claim 66 wherein the photocatalytic titanium oxide particles consists essentially of

titanium dioxide in the anatase crystalline form.

20 68. The photocatalytic aggregate particle according to claim 66 wherein the photocatalytic titanium oxide particles are less than about 20% by weight.

69. The photocatalytic aggregate particle according to claim 66  
25 wherein the extender particle is a material drawn from the group consisting essentially of silicates and carbonates including silicate and carbonate powders, mineral and mineral composites

including calcined clay and wollastonite, metal oxides including zinc oxide, inorganic pigments, and construction aggregates including roofing granules.

- 5 70. A process of making photocatalytic aggregate particles comprising:

mixing an aqueous slurry of

extender particles made from material both non-  
photocatalytic and non-interfering with photocatalytic reactions  
10 with

a solution of titanyl sulfate; then

adding an acid or an alkaline reacting agent to cause  
discrete microparticles of titanium dioxide to be deposited onto  
the extender particles.

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71. A process for making photocatalytic aggregate particles comprising:

mixing an aqueous slurry of

extender particles made from material both non-  
20 photocatalytic and non-interfering with photocatalytic reactions  
with

an alkaline or acidic titania sol containing particles  
of titanium dioxide.

- 25 72. The process for making photocatalytic aggregate particles according to claim 71 wherein the titanium dioxide particles in the titania sol have an average diameter size within the range of



about 1 to about 100 nanometers.

73. The process for making photocatalytic aggregate particles according to claim 71 wherein the titanium dioxide particles in  
5 the titania sol and the extender particles are both above or below their respective isoelectric points.

74. The process for making photocatalytic aggregate particles according to claim 71 wherein discrete particles of the titanium  
10 dioxide that is within the titania sol are dispersed onto the surfaces of the extender particles in an amount less than 20 weight % based on aggregate particle weight.